

CHEMICALLY DEPOSITED

CdS-Cu<sub>x</sub>S SOLAR CELLS

by

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## PREFACE

The cadmium sulfide-cuprous sulfide ( $\text{CdS-Cu}_x\text{S}$ ) solar cell has future promises as a low cost solar energy device. In this study, low efficiency  $\text{CdS-Cu}_x\text{S}$  photoelectric cells were fabricated from chemically deposited (aqueous solution) cadmium sulfide thin films. Considerable experience was gained in solar cell technology and in the modern techniques used to characterize thin film semiconductors. Also, valuable knowledge was acquired from the chemistry of thin film deposition.

I would like to gratefully thank my acting advisor, Dr. R. L. Call for his helpful suggestions. I am also gratefully indebted to Dr. K. Seshan and Mr. J. Whyte for their valuable assistance in using the X-ray and transmission electron microscope. Kindest thanks are also due Dr. Fordemwalt for his helpful advice.

## TABLE OF CONTENTS

	Page
LIST OF ILLUSTRATIONS . . . . .	vi
LIST OF TABLES. . . . .	vii
ABSTRACT. . . . .	viii
1. INTRODUCTION. . . . .	1
Cell Parameters . . . . .	1
Equivalent Circuit. . . . .	3
Energy Band Diagram . . . . .	5
Photogeneration and Grain Boundaries. . . . .	7
2. THE TECHNIQUES FOR THE CHEMICAL DEPOSITION OF CdS . . . . .	11
Introduction. . . . .	11
The Conventional Method . . . . .	11
Deposition from an Ammonium Nitrate Solution of Cadmium . . . . .	12
Deposition from Cyanide Solution. . . . .	13
Heat Treatment and Chemical Doping. . . . .	14
3. THE CHEMICAL DEPOSITION OF ZnO. . . . .	17
Introduction. . . . .	17
Preparation Procedure . . . . .	17
X-Ray Diffraction Results . . . . .	18
Sheet Resistivity Measurements. . . . .	18
Conclusion and Recommendation . . . . .	18
4. THE CRYSTALLINE PROPERTIES OF THE CHEMICALLY DEPOSITED CdS FILMS . . . . .	21
Introduction. . . . .	21
X-Ray Diffraction Results . . . . .	21
Transmission Electron Microscopy Results. . . . .	26
Conclusion. . . . .	28
5. METHODS OF FABRICATING THE CdS-Cu <sub>x</sub> S SOLAR CELLS . . . . .	30
Experimental Procedure. . . . .	30
The CuCl Dipping Solution . . . . .	31
Experimental Results. . . . .	32

## TABLE OF CONTENTS--Continued

	Page
6. CONCLUSIONS AND RECOMMENDATIONS. . . . .	37
Improvement of the Solar Cells . . . . .	37
Discussion of Results on Impurity Analyses . . . . .	38
Guidelines for Further Study . . . . .	39
REFERENCES . . . . .	42

## LIST OF ILLUSTRATIONS

Figure	Page
1. Cross-sectional diagram of a CdS-Cu <sub>x</sub> S solar cell. . . . .	2
2. An electrical equivalent circuit of a solar cell. . . . .	4
3. An I-V curve of a typical solar cell under illumination . .	6
4. Energy band diagram of a CdS-Cu <sub>x</sub> S hetero-junction . . . . .	8
5. Cross-sectional diagram of grain boundaries . . . . .	9
6. The effect of excess KCN on the temperature of deposition of CdS from cyanide solution. . . . .	15
7. X-ray diffraction pattern of ZnO thin films deposited from solution . . . . .	19
8. X-ray diffraction pattern of CdS deposited from the conventional ammonium solution. . . . .	22
9. X-ray diffraction pattern of CdS deposited from a solution of cadmium in ammonium nitrate. . . . .	23
10. X-ray diffraction pattern of CdS films deposited from KCN solution and annealed in air at 250°C . . . . .	24
11. X-ray diffraction pattern of CdS deposited from the conventional solution using thioacetamide as the sulfiding agent . . . . .	25
12. An electron diffraction pattern showing the three impurity peaks . . . . .	27
13. An electron photomicrograph of grain sizes. . . . .	29
14. I-V curves of two chemically deposited solar cells under 1 sun illumination. . . . .	35

LIST OF TABLES

Table		Page
1.	A comparison between chemically deposited solar cells. . . .	36
2.	Atomic absorption results on CdS deposited from a solution of Cd in ammonium nitrate . . . . .	38
3.	SEMQ results on CdS deposited from a solution of Cd in $\text{NH}_4\text{NO}_3$ . . . . .	39

## ABSTRACT

The physical properties of cadmium sulfide and zinc oxide thin films, deposited from aqueous solution, were investigated using electron and x-ray diffraction techniques. The conventional method and two new methods were used to deposit cadmium sulfide thin films. Moreover, a new method for the deposition of zinc oxide was devised. Experiments were conducted on the cadmium sulfide thin films in order to make their semiconducting properties favorable for use as solar cells. CdS-Cu<sub>x</sub>S solar cells were fabricated, and their I-V characteristic curves plotted, using an X-Y recorder. The photovoltaic effects in chemically deposited CdS films have been clearly demonstrated.

## CHAPTER 1

### INTRODUCTION

The cadmium sulfide-cuprous sulfide photovoltaic cell (CdS-Cu<sub>x</sub>S) is a device which transforms light energy to electric energy. Typically, this cell is composed of four basic elements as shown in Figure 1. A p-n junction is formed between cadmium sulfide (n-type) and cuprous sulfide (p-type). Two ohmic contacts are attached to both sides of the junction. One of the ohmic contacts is transparent or has a grid structure in order to allow the light penetration into the junction. The structure illustrated in Figure 1 is termed front wall because light rays are incident on the Cu<sub>x</sub>S side of the cell.

#### Cell Parameters

A solar cell is commonly described through three main parameters, the short circuit  $I_{sc}$ , open circuit voltage  $V_{oc}$ , and curve fill factor CFF, which are interrelated by equations (1) and (2),

$$V_{oc} = C_d \frac{kt}{q} \ln \left[ \frac{I_{sc}}{I_D} + 1 \right] \quad (1)$$

$$CFF = \frac{V_m I_m}{V_{oc} I_{sc}} \quad (2)$$

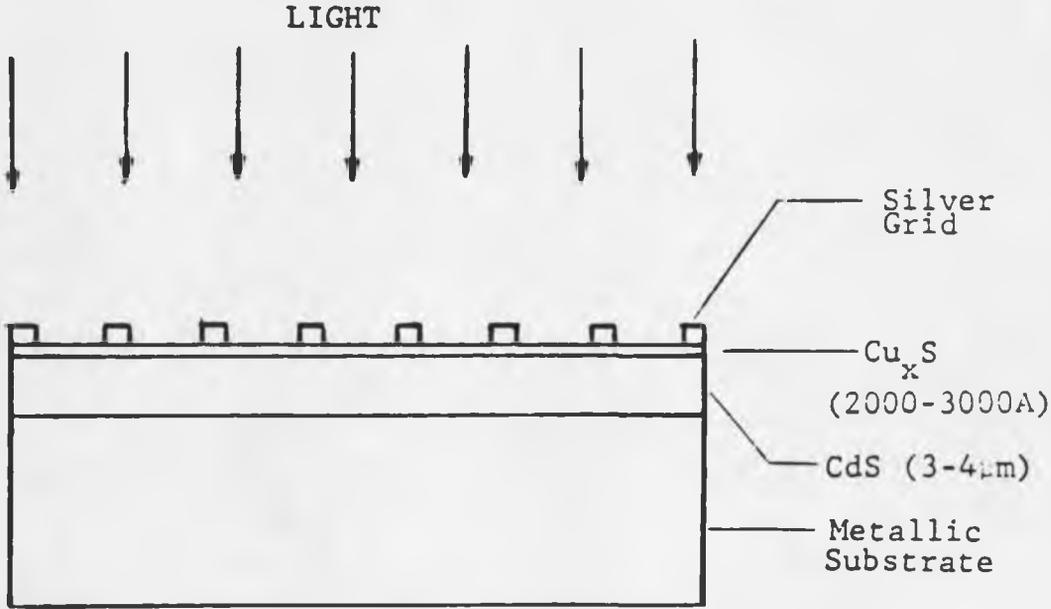


Figure 1. Cross-sectional diagram of a CdS- $\text{Cu}_x\text{S}$  solar cell.

The product  $V_m I_m$  is the maximum power output of the cell and  $C_d = 1$  for an "ideal" junction. The dark current  $I_D$  is usually of the order of  $1 \times 10^{-14}$  ma and increases with increasing  $C_d$ , which will result in lower values of  $V_{oc}$ .  $V_m$  and  $I_m$  are the voltage and current at the maximum power point.  $V_{oc}$  and  $I_{sc}$  are the open circuit and short circuit voltage and current respectively. CFF is termed the curve fill factor.  $T$  is the temperature in degrees Kelvin,  $k$  is the boltzman constant and  $q$  is the electron charge.

Equations (3), (4) and (5) can be easily derived from equations (1) and (2),

$$I_m = \frac{-\beta V_m (I_{sc} + I_D)}{1 + \beta V_m} \quad (3)$$

$$V_{oc} = V_m + \frac{1}{\beta} \ln(\beta V_m + 1) \quad (4)$$

$$CFF = \frac{V_m^2 \beta (I_D + I_{sc})}{I_D V_{oc} (1 + \beta V_m) (e^{\beta V_{oc}} - 1)} \quad (5)$$

whereby,  $\beta = \frac{q}{kt}$ .

#### Equivalent Circuit

An equivalent circuit of a photo cell is shown in Figure 2. This circuit is composed of a series resistance  $R_s$ , a shunt resistance  $R_{sh}$ , a current source  $I_L$ , and the diode of the junction. These elements are interrelated by equation (6),

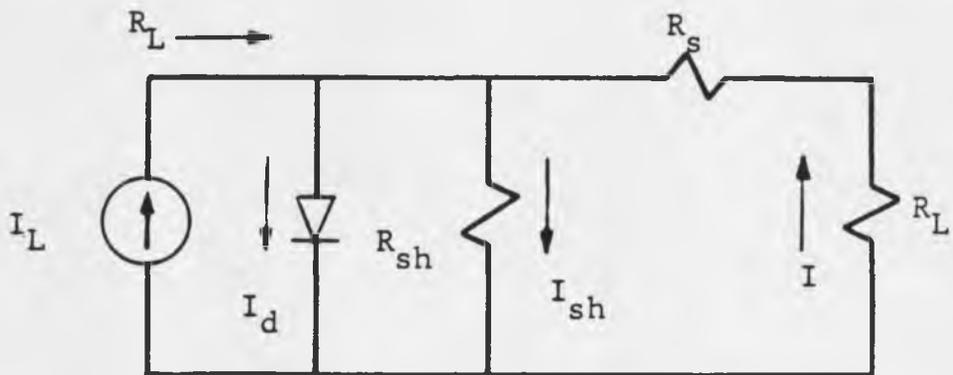


Figure 2. An electrical equivalent circuit of a solar cell.

$I_L$  is an ideal current source and  $R_L$  is a load resistance.

$$I = I_d \left\{ e^{(V-IR_s)/R_{sh}} - 1 \right\} - I_L + \frac{V-IR_s}{R_{sh}} \quad (6)$$

Simple circuit analysis shows that the load current supplied to  $R_L$  is inversely proportional to  $R_s$  and  $R_{sh}$ . The series resistance  $R_s$  is dependent on the resistivity of the bulk material of the solar cell through which the majority carriers have to migrate before reaching the ohmic contacts.

Solar cells are usually described by their curve fill factor which can be deduced graphically from the I-V characteristic curve of the cell. Figure 3 illustrates the I-V curve for an ideal solar cell, and  $P_m$ , the maximum power point, is graphically located at the knee of the curve. The closer the I-V curve resembles a square shape, the more efficient the cell is.

#### Energy Band Diagram

Principally, under illumination, the solar cell forward biases its own diode. Electron hole pairs are generated when absorbed photons have energies greater than the band energy. If the minority carriers reach the junction before they recombine, they will be swept across the junction by the effect of the depletion electric field. The flow of these carriers across the junction gives rise to a photogenerated electric field which is opposite in direction to the depletion region electric field. Thus, the barrier height across the junction is lowered, making it easier for photogenerated carriers to migrate. In the case of a photocell with a heterojunction ( $CdS-Cu_xS$ ), a potential

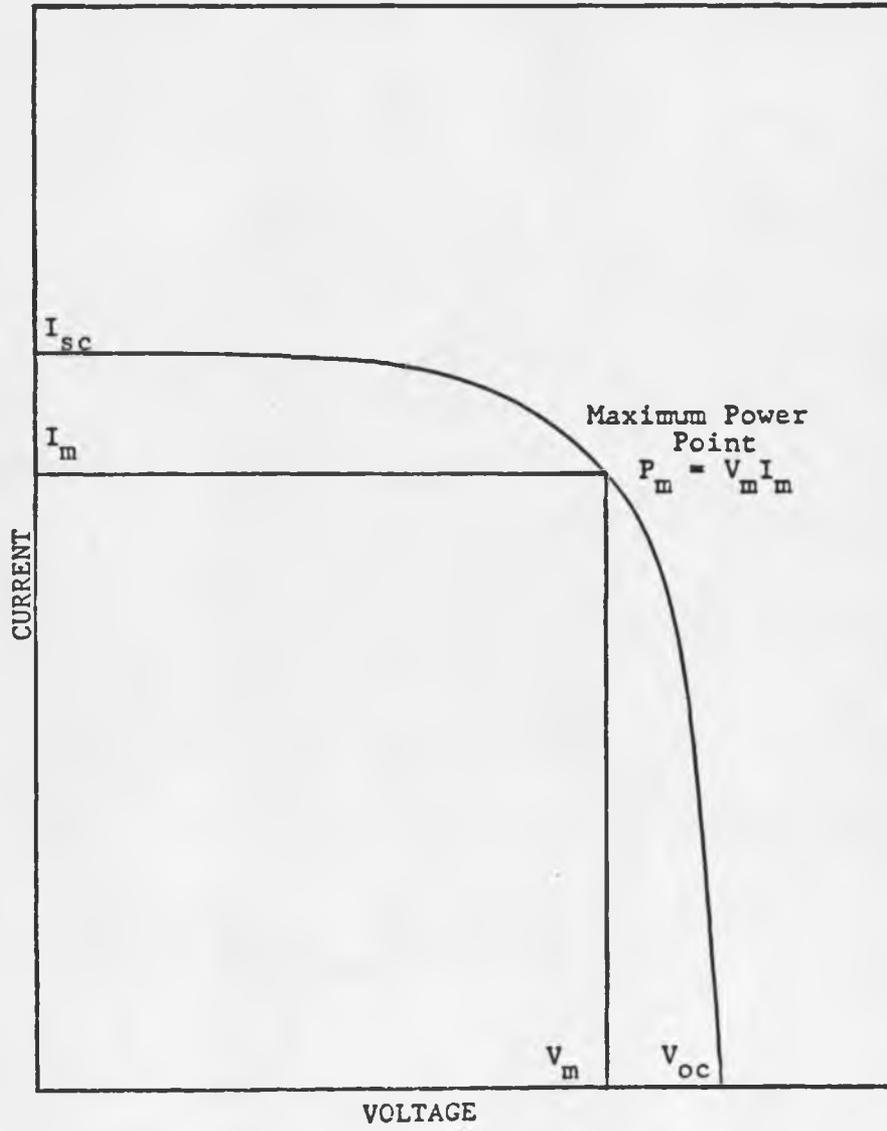


Figure 3. An I-V curve of a typical solar cell under illumination.

barrier "B" exists due to Cu acceptors which diffuse into the bulk CdS after heat treatment. Figure 4 illustrates an energy band diagram of the CdS-Cu<sub>x</sub>S heterojunction.<sup>1</sup>

#### Photogeneration and Grain Boundaries

For a single crystalline p-n junction, the photogenerated current can be calculated by solving the continuity and diffusion equations using two boundary conditions. However, for a polycrystalline p-n junction, the situation is more complicated, because no detailed study of the grain boundary effects on photocurrent has been carried out. To calculate the photogenerated current for CdS-Cu<sub>x</sub>S solar cell would require solving a three-dimensional diffusion equation with eight boundary conditions.

Grain boundaries have severe effects on the photocurrent of a solar cell. By acting as minority carrier recombination centers and majority carrier barriers, they reduce the photogenerated currents, increase series resistance and decrease shunt resistance. Figure 5a shows a cross-sectional diagram of grain boundaries which do not have any orientational structure. The grains of upper layer will mostly contribute to the photogenerated current, while the grain boundaries separating the upper from the lower grains, will act as minority carrier sinks and majority carrier high resistance barriers. A more favorable structure is shown in Figure 5b, where the grains have a fibrous orientation. In this case, recombination losses occur mainly along the vertical boundaries. Carriers generated in each grain will diffuse down to the junction without encountering the barriers and sinks.

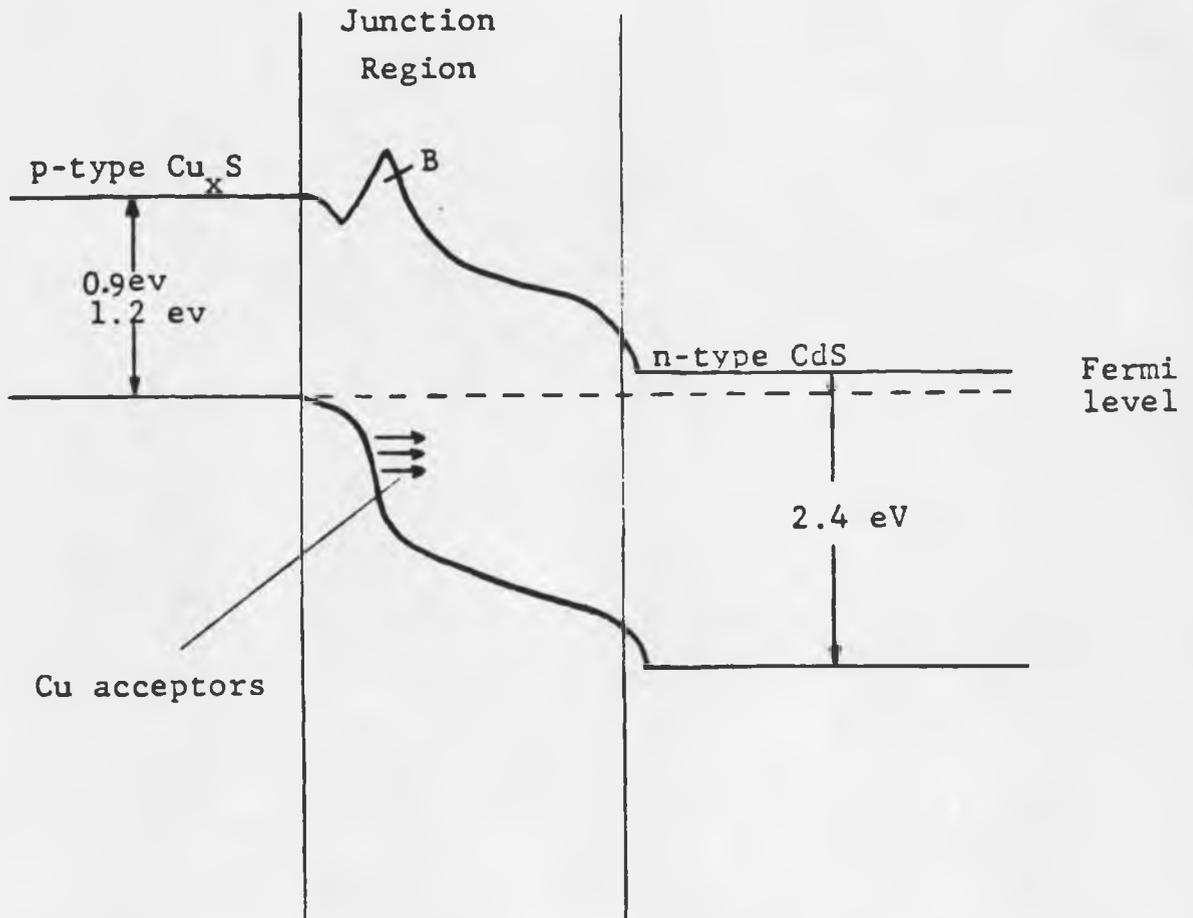
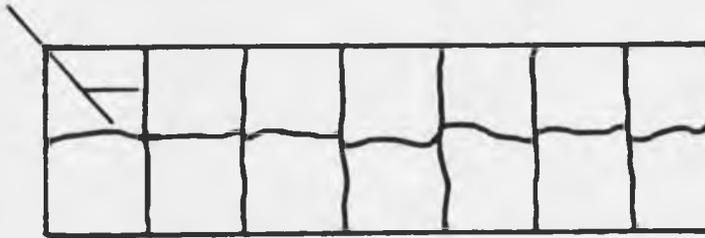
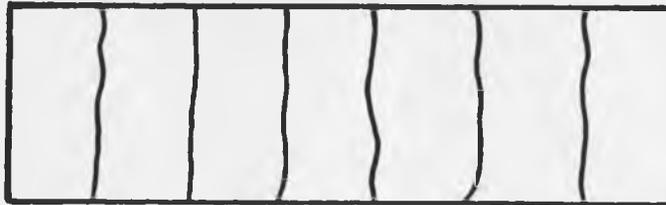


Figure 4. Energy band diagram of a CdS-Cu<sub>x</sub>S heterojunction.

Grain Boundaries



- (a) Grains with orientation along the various axes of the crystallite structure.



- (b) Fibrous structure of grains oriented along the c-axis of the substrate.

Figure 5. Cross-sectional diagram of grain boundaries.

Photogenerative layers of  $\text{Cu}_x\text{S}$  that have this fibrous structure are more favorable for the fabrication of solar cells because recombination losses can be greatly reduced by increasing the grain size to an order of magnitude of the diffusion length  $L$  of the carriers.<sup>2</sup> In other words, the wider the fibers (increasing grain size) are, the lesser the chances are of an electron hole pair recombining at the grain boundaries. In CdS solar cells, the optimum thickness of the  $\text{Cu}_x\text{S}$  layer is 2000-3000A where 99% of photogeneration occurs. A general rule for efficient carrier collection is to have the grain size greater than or equal to the thickness of the  $\text{Cu}_x\text{S}$  layer.

As will be seen in the next chapter, cadmium sulfide films were deposited by three techniques. Two of these techniques yielded films having the structure of Figure 5a, while the third (from cyanide solution) yielded films having crystalline structure similar to Figure 5b. This latter structure was confirmed by x-ray diffraction techniques. As expected, the KCN-method yielded the cells with the highest conversion efficiencies.

## CHAPTER 2

### THE TECHNIQUES FOR THE CHEMICAL DEPOSITION OF CdS

#### Introduction

Thin films of cadmium sulfide were deposited on glass slides from aqueous solutions, using three techniques: two new and one conventional. These techniques are based on one major principle, complexing the cadmium ions with either an ammonium salt or an alkali cyanide and then using thiourea as a sulfiding agent.

#### The Conventional Method

The first method used to deposit cadmium sulfide is conventional and has been reported by others.<sup>3,4</sup> Sodium or potassium hydroxide is added to a cadmium salt to form a cadmium hydroxide precipitate. An ammonium salt is then added to dissolve this precipitate and to form a cadmium amine complex. Deposition proceeds when thiourea is added to the clear solution. The thin films which were studied here were deposited by adding equal volumes of 0.5M NaOH, 0.1M  $\text{Cd}(\text{NO}_3)_2$  and 0.1M  $\text{CS}(\text{NH}_2)_2$ . Ammonium nitrate (50 g/100 cc) was used to dissolve the cadmium hydroxide precipitate and the solution was heated to 90°C. Best results were obtained when the quantity of ammonium nitrate used was just enough to dissolve the cadmium hydroxide. Excessive addition of the ammonium salt served to slow down the deposition or even completely stop it.

However, when thioacetamide was used as the sulfiding element, excessive addition of ammonium nitrate did not affect the deposition. On the contrary, deposition proceeded at room temperature, and thin films with interesting properties were obtained.

This method of deposition yielded thin films the thickness of which varied from  $1000\text{\AA}$  -  $2000\text{\AA}$ . The thicknesses were measured from evaporated aluminum steps on the layers. Multiple depositions were found to yield thicknesses greater than  $1\ \mu\text{m}$ . This method has one major disadvantage. During heating, and before deposition starts, large white granules of  $\text{Cd}(\text{OH})_2$  are formed, which act as nucleons. Most of the deposited CdS grow on these nucleons causing the formation of clogs. The solution then breaks into turbidity, which has adverse effects on the yield and uniformity of the thin films. This problem can be partially resolved by adding thiourea, drop by drop, or by using thioacetamide as a sulfiding agent.

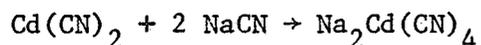
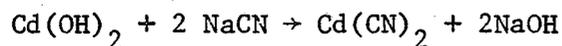
#### Deposition from an Ammonium Nitrate Solution of Cadmium

Cadmium metal dissolves at room temperature in an aqueous solution of ammonium nitrate. The nature of the chemical reaction is not well understood. Hodgekinson and Coote<sup>5</sup> reported when cadmium dissolves in an aqueous solution of  $\text{NH}_4\text{NO}_3$ , free ammonia is liberated and cadmium nitrate is formed. However, H. Morin<sup>6</sup> reported different results. He stated that cadmium dissolves in ammonium nitrate to give a complex of cadmium ammonium nitrate.

When thiourea is added to an aged solution of cadmium in ammonium nitrate, a thin film of CdS is formed on suitable substrates such as glass, molybdenum, aluminum and zinc. The concentration of ammonium nitrate most suitable for deposition of CdS was found to vary from 0.3M-1.0M. Best results were obtained when 0.3M  $\text{NH}_4\text{NO}_3$  (in which cadmium was introduced) was aged for three days. The thickness of the thin films deposited was found to increase with aging time. Also, uniformity and adhesion was found to be appreciably improved when the substrates were left in the solution for one hour. The films prepared this way were light yellow and nontransparent. By adding thiourea drop by drop, transparent films were obtained on glass.

#### Deposition from Cyanide Solution

In this method, cadmium hydroxide is dissolved by using sodium or potassium cyanide instead of ammonium salt. L. R. Westbrook<sup>7</sup> observed that cadmium hydroxide or cadmium oxide reacts with sodium cyanide to form sodium hydroxide and cadmium cyanide, which dissolves in the excess sodium cyanide present to form sodium cadmium cyanide, a complex compound termed disodium tetracyano-cadmiate.



Cadmium hydroxide was freshly precipitated by mixing equal volumes of 0.5M  $\text{Cd}(\text{NO}_3)_2$  and 0.5M KOH. Then potassium cyanide was added directly

in granular form to dissolve the cadmium hydroxide and all other precipitates. Thiourea was used in diluted form to deposit CdS thin films on glass, molybdenum, copper, and nickel substrates. Heating was necessary to start the deposition ( $T \geq 80^\circ\text{C}$ ). Optimum results were obtained when all the precipitates were dissolved. Adding excess KCN did not cause noticeable effects on the thickness of the films. However, the temperature of deposition was found to increase with the addition of excess KCN after the dissolution of the precipitates. Figure 6 illustrates the temperature variation in terms of percent (by weight) excess KCN added to the solution after the precipitates had just dissolved. The percentage values were taken as the ratio of excess weight of KCN to that needed to just dissolve the precipitates. It was found that when the quantity of excess KCN added exceeds 25% of that required to just dissolve the precipitates, the deposition will require a temperature of deposition greater than  $100^\circ\text{C}$ . The temperature of deposition was decreased by adding excess NaOH, but the films were less uniform and less adhesive.

#### Heat Treatment and Chemical Doping

CdS films prepared by multiple depositions from the three different solutions (thickness =  $1.0\text{-}2.0\ \mu\text{m}$ ) exhibited high sheet resistivities ( $R = 10^6\text{-}10^8\ \Omega/\square$ ) as determined by a four point probe apparatus. It was observed that when some chemical compounds were introduced into the solution, during deposition, films with lower sheet resistivities were obtained. CdS deposited by the conventional

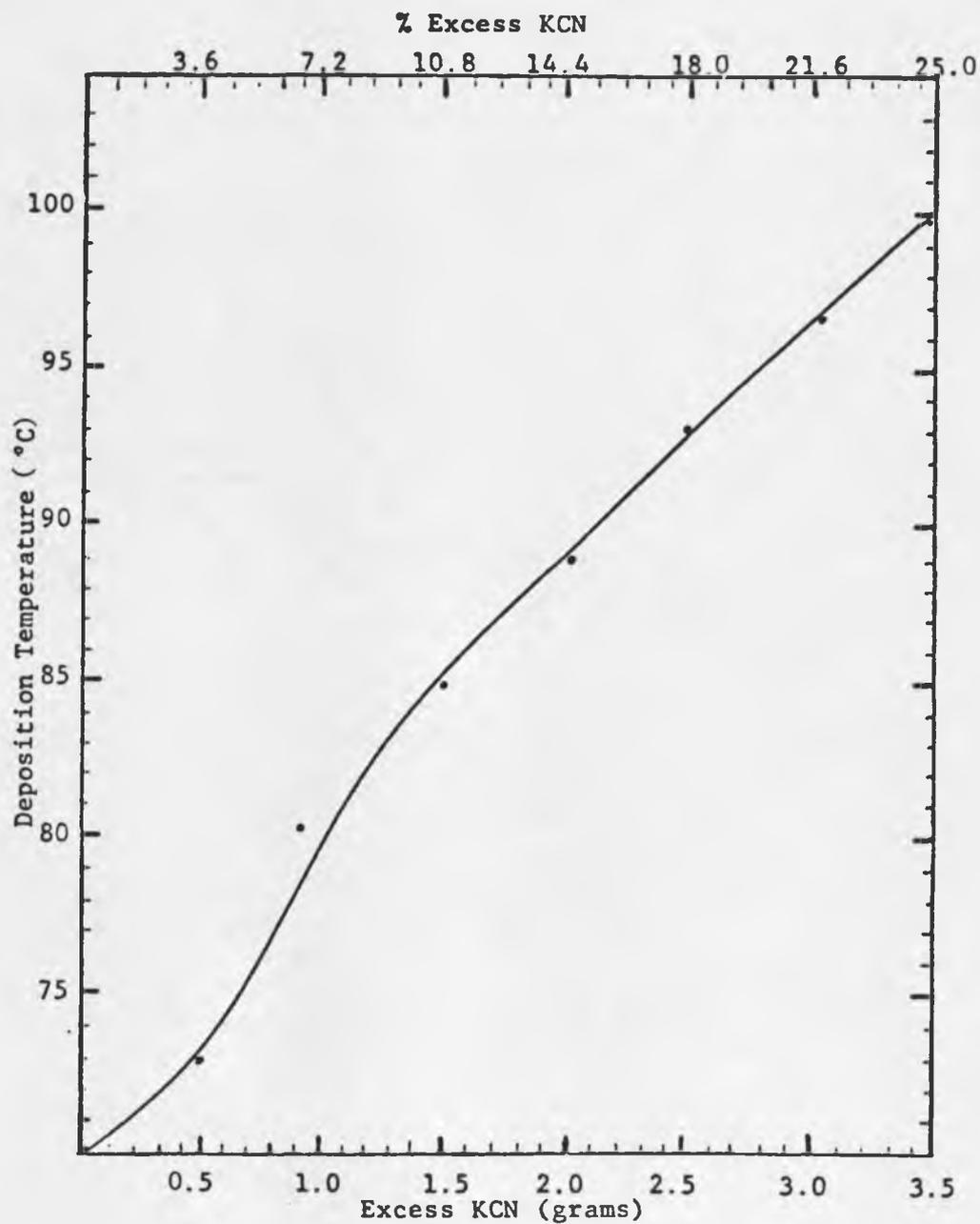


Figure 6. The effect of excess KCN on the temperature of deposition of CdS from cyanide solution.

method exhibited lower sheet resistivities,  $R_s \approx 10^5 \Omega/\square$ , when a few drops of 0.1M KCN were added. The introduction of lead, zinc or mercury salts exerted marked changes on the physical properties of the films.

Heat treating the CdS films in oxidizing or reducing atmospheres was observed to also decrease their sheet resistivities. Films deposited from the cyanide solution displayed relatively lower sheet resistances  $R_s = 10^4 - 10^5 \Omega/\square$  when they were annealed in air at  $250^\circ\text{C}$  for a few minutes. A hot point probe test indicated n-type conductivity on heat treated films prepared by two or more multiple depositions. Films deposited from cadmium ammonium nitrate solution showed similar behavior when annealed in 10%  $\text{H}_2$ , 90%  $\text{N}_2$  at  $360^\circ\text{C}$  for five minutes. The sheet resistance varied from  $10^4 - 10^5 \Omega/\square$ . In addition, these films were observed to permanently change in color from yellow to orange after annealing. No marked changes were noticed on heat treated CdS film deposited by the conventional method.

It is believed that when CdS is annealed in hydrogen, some of the sulfide ions react with the reducing gas to form  $\text{H}_2\text{S}$ . Thus, acceptors are taken away, leaving free electrons which make the CdS n-type. The effect of annealing in air on the CdS films deposited from cyanide solution is not well understood.

## CHAPTER 3

### THE CHEMICAL DEPOSITION OF ZnO

#### Introduction

The introduction of zinc salts into the CdS depositing solutions was thought to yield a CdS-ZnS system. However, x-ray diffraction techniques on these films showed the presence of ZnO impurities. Further experiments led to the development of a new technique for the deposition of ZnO.

#### Preparation Procedure

Freshly deposited precipitates of zinc hydroxide were found to dissolve readily in cold potassium cyanide solution. When the clear solution was heated, a white precipitate of ZnO was formed. Only concentrated solutions of  $\text{Zn(OH)}_2$  were observed to yield adhesive ZnO films on glass slides. Optimum results were obtained when the zinc hydroxide precipitate was prepared by adding 0.5M NaOH and 1.0M  $\text{ZnSO}_4$  at room temperature. KCN in granular form was added slowly until all the precipitates were dissolved. Heating of the cold solution at 80°C to 90°C was essential to start the deposition. The thickness of the films varied from 0.2-0.4  $\mu\text{m}$ . A second deposition on these films was found to yield more uniform and adhesive films with thicknesses up to 1.5  $\mu\text{m}$ . It is believed that an initial coating of ZnO on the glass

substrate acts as a thin seeding layer which initiates much faster film growth upon a second dip.

The nature of the chemical reaction is not well understood. An alkali cyano zincate complex is thought to form when KCN and  $\text{Zn(OH)}_2$  are mixed. Upon heating, the zincate ( $\text{ZnO}_4^{--}$ ) radical separates and because of its high stability the zinc oxide forms. This behavior was not observed in  $\text{Cd(OH)}_2$  cyanide solutions. Tin oxide was deposited by a similar chemical interaction between KCN and  $\text{SnO}_3^{--}$ . However, the thin films were not very adhesive and no definite results have been obtained.

#### X-Ray Diffraction Results

X-ray diffraction techniques were conducted on four ZnO samples prepared by 2-3 multiple depositions. Figure 7 shows a typical x-ray diffraction pattern obtained with a Cu target ( $\lambda=1.54$ ). The polycrystalline structure of the films is hexagonal with preferential growth along the (100) direction.

#### Sheet Resistivity Measurements

The sheet resistivity of the films was in the vicinity of  $10^8 \Omega/\square$ . Some of the samples exhibited lower resistivities  $10^4$ - $10^5 \Omega/\square$  and n-type conductivity upon annealing in 10%  $\text{H}_2$ , 90%  $\text{N}_2$  at  $350^\circ\text{C}$  for a few minutes.

#### Conclusion and Recommendation

A potential evaluation of the ZnO thin films prepared by the technique described in this chapter cannot be done because the physical study which was carried out was very brief. However, this new technique of deposition should be fully investigated in order to understand the

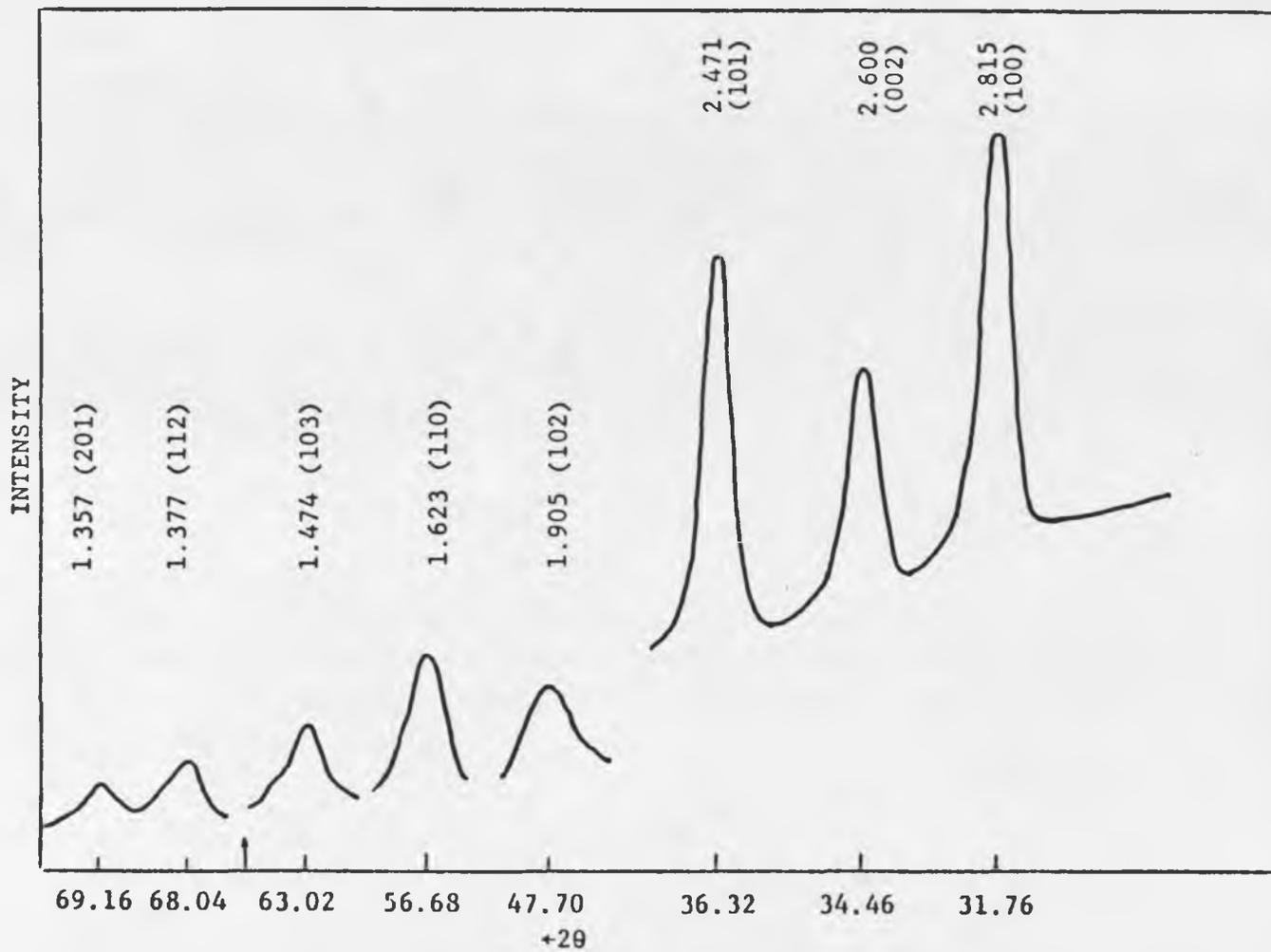


Figure 7. X-ray diffraction pattern of ZnO thin films deposited from solution.

chemical reaction that takes place in the solution. This may lead to the utilization of the method for the deposition of some other metallic oxides.

## CHAPTER 4

### THE CRYSTALLINE PROPERTIES OF THE CHEMICALLY DEPOSITED CdS FILMS

#### Introduction

X-ray diffraction techniques (XRD) were used to characterize the crystalline structure of the CdS films. Transmission Electron Microscopy (TEM) was conducted on CdS samples deposited from the cadmium in ammonium nitrate solution.

#### X-Ray Diffraction Results

X-ray diffraction patterns of CdS films deposited by the three methods are shown in Figures 8, 9, 10 and 11. The films were deposited on glass substrates and multiple depositions were necessary to obtain a thickness of 1  $\mu\text{m}$ . A Cu target was used ( $\lambda=1.54\text{\AA}$ ). X-ray diffraction techniques have shown that the crystalline structure of all the films is hexagonal. Crystallites exhibited preferential orientational growth along the (002) axis (C-axis). This preferential growth is clearly demonstrated in CdS freshly precipitated from KCN solution, where orientational growths along other axis are absent. However, as Figure 10 shows, growths along the other axis were activated by annealing in air at 250°C for ~15 minutes.

Films deposited by the Cd-NH<sub>4</sub>NO<sub>3</sub> method contain impurities of unknown composition. Figure 9 illustrates the existence of these

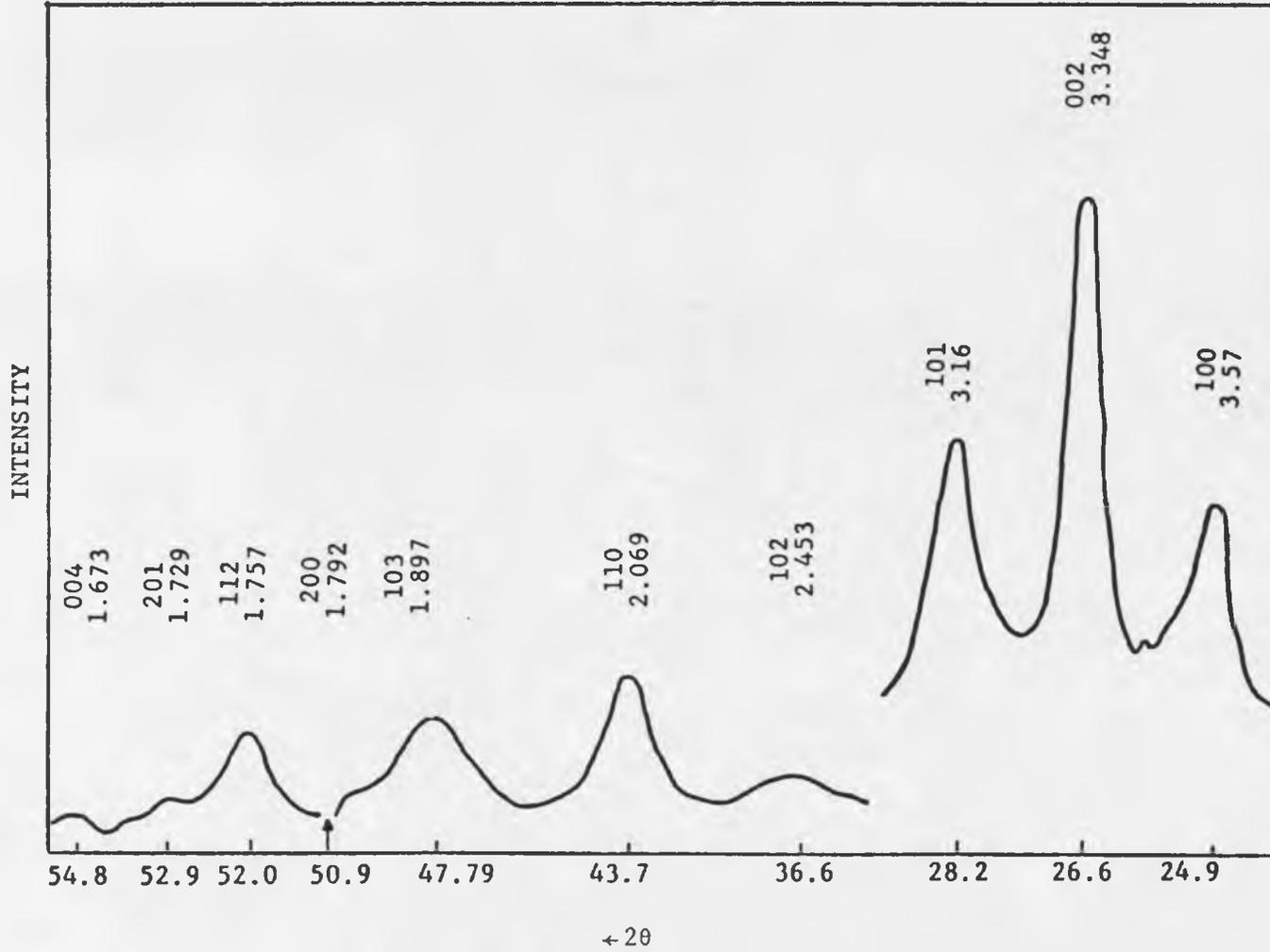


Figure 8. X-ray diffraction pattern of CdS deposited from the conventional ammonium solution.

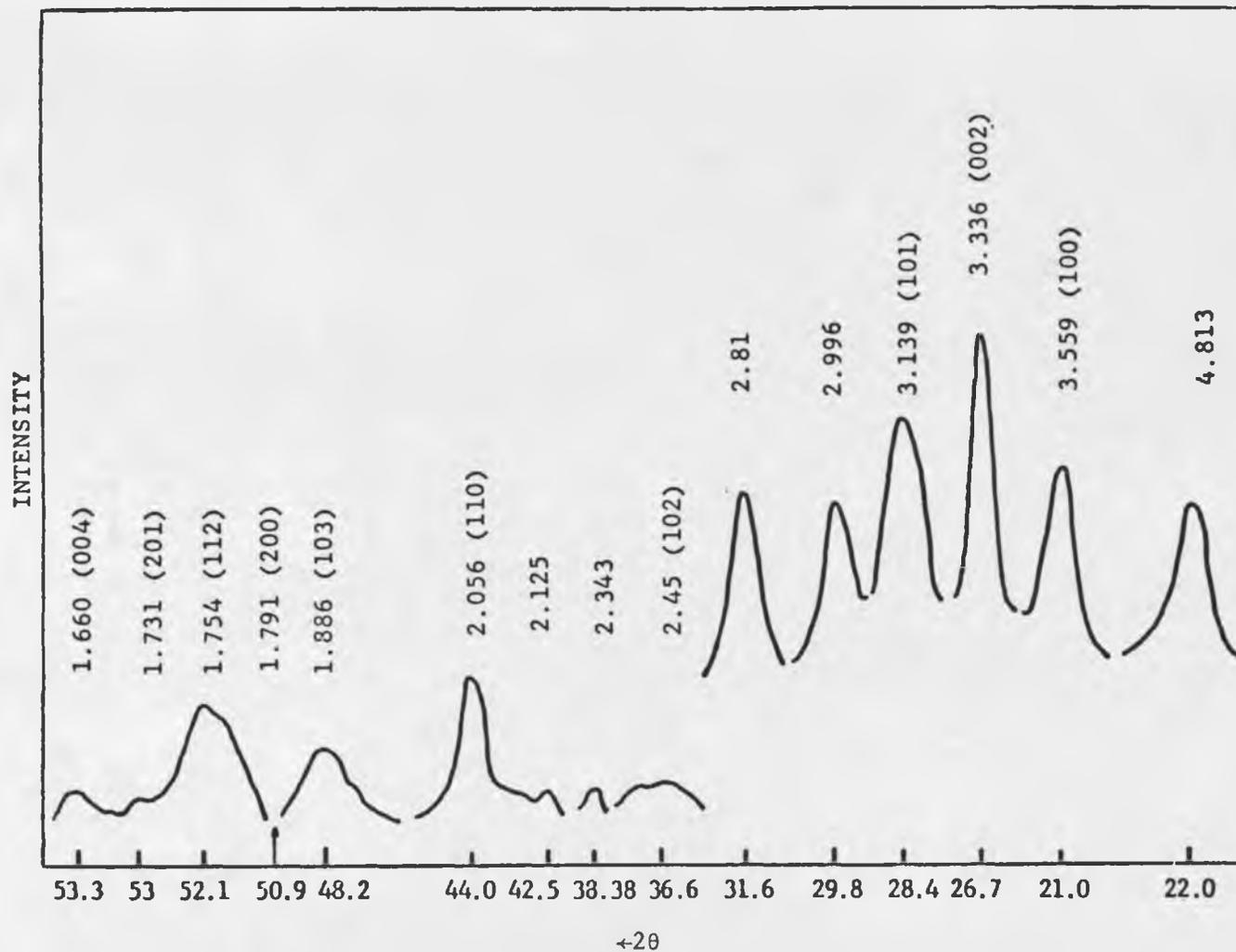


Figure 9. X-ray diffraction pattern of CdS deposited from a solution of cadmium in ammonium nitrate.

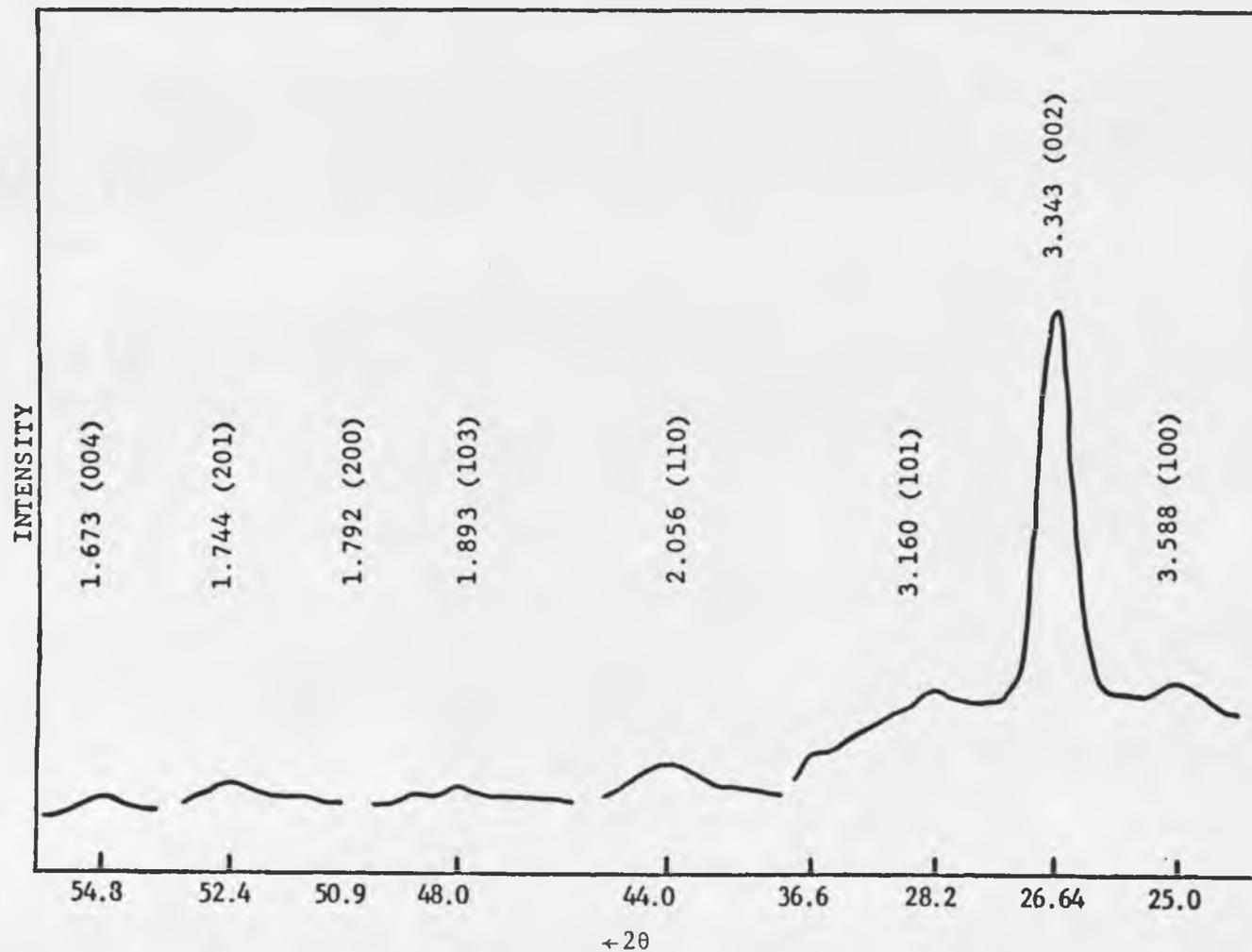


Figure 10. X-ray diffraction pattern of CdS films deposited from KCN solution and annealed in air at 250°C.

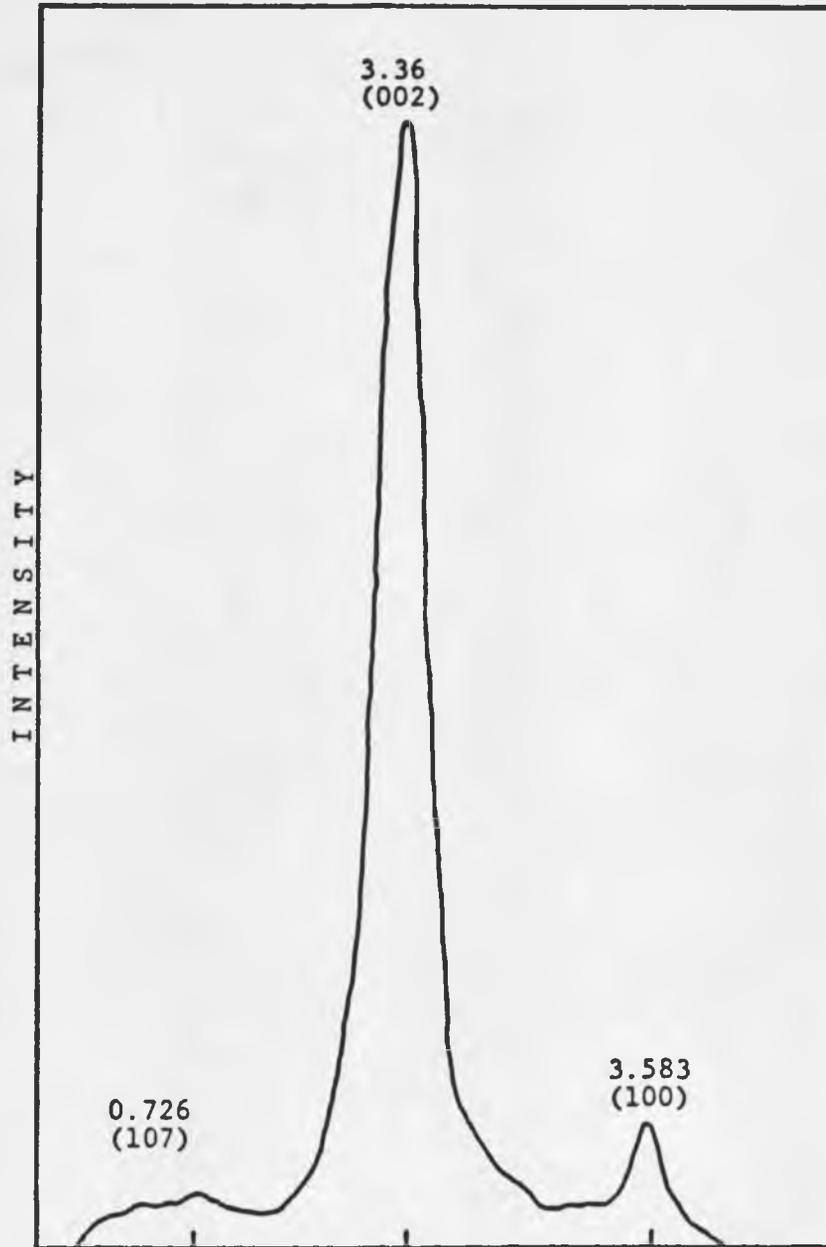


Figure 11. X-ray diffraction pattern of CdS deposited from the conventional solution using thioacetamide as the sulfiding agent.

impurities through three large peaks ( $d=4.183$ ,  $d=2.996$ ,  $d=2.81$ ) and two small peaks ( $d=2.343$ ,  $d=2.125$ ). These do not belong to either hexagonal or cubic CdS. One common characteristic which was observed in all the films was the absence of growth along the (200) axis.

It was observed that the  $d$ -spacings of the thin films were slightly different from those listed in the standard reference charts. This variation is related to stresses that exist in the lattices.

To illustrate the importance of the sulfiding agent used, thioacetamide was added to an ammonium solution prepared by the conventional method. Figure 11 illustrates an x-ray radiogram on films deposited at room temperature. The growth along the  $c$ -axis with the growths along the other axis partially or completely abolished is clearly seen. The sharpness of the (002) peak indicates larger grain sizes than those deposited by the other methods which use thiourea as a sulfiding agent.

#### Transmission Electron Microscopy Results

Transmission electron microscopy was used to further characterize CdS films deposited from aged cadmium-ammonium nitrate solution. These films were particularly interesting because x-ray diffraction techniques revealed the existence of three, large, unidentified peaks at  $d$ -spacing of 4.183, 2.996 and 2.81 (see Figure 9). The results obtained were in agreement with the x-ray diffraction graphs. Figure 12 illustrates a diffraction pattern of an electron-beam-irradiated CdS film. The sample



Figure 12. An electron diffraction pattern showing the three impurity peaks.

was prepared from powders scraped off a 0.4  $\mu\text{m}$  film on a glass substrate. The d-spacings were calculated from the relation

$$\lambda L = rd$$

where  $\lambda L = 1.83$  for aluminum taken as reference. The values of d were observed to agree with those of the XRD results in Figure 9, which confirms the hexagonal structure of the films. The three non-CdS rings were observed at radii of 0.38, 0.61 and 0.65 cm, which confirms the existence of an unknown material.

Figure 13 illustrates an electron micrograph of the grain sizes which were estimated to vary from 100-400 $\text{\AA}$ . The value is in agreement with that estimated from the XRD diffraction techniques.

### Conclusion

XRD and TEM techniques have confirmed the existence of a polycrystalline material foreign to CdS. The actual chemical composition of this material has not been identified yet. Atomic Absorption Analysis have shown that the content of nitrogen is 6%, but it has failed to determine the content of oxygen and sulfur. So, no conclusive identification of the impurity material is possible from this analysis.

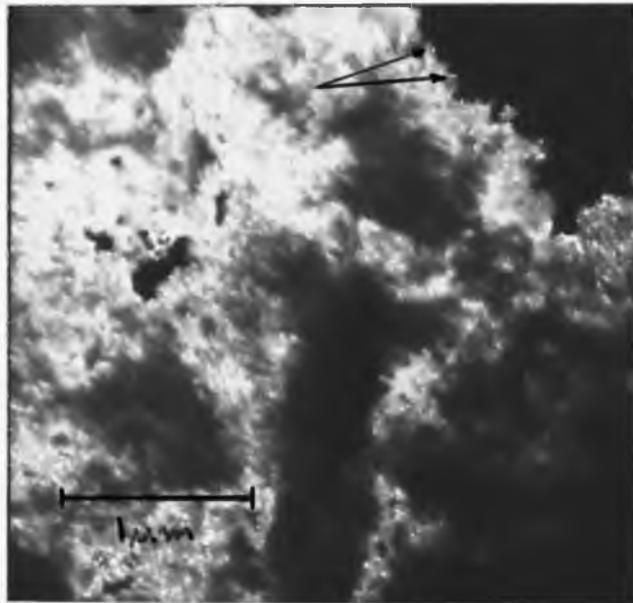


Figure 13. An electron photomicrograph of grain sizes.

## CHAPTER 5

### METHODS OF FABRICATING THE CdS-Cu<sub>x</sub>S SOLAR CELLS

#### Experimental Procedure

A chemical barrier formation process developed earlier was used to fabricate the CdS-Cu<sub>x</sub>S photocells. The surface of the CdS film is treated with a CuCl solution to form a photoelectric p-n junction. The following steps were carried out in fabricating the cells:

1. Surface polishing of a metallic substrate which is insoluble in depositing solution.
2. Several dips in the CdS depositing solution to obtain a layer thickness of 3-4  $\mu\text{m}$ .
3. Dip for 4-6 seconds in hot, saturated (99°C) CuCl solution.
4. Heat treatment of the cell at 250°C in air for 20-60 seconds.
5. Application of a silver grid on top of the Cu<sub>x</sub>S layer.

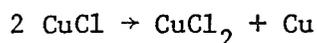
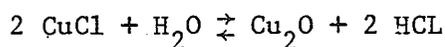
Heat treatment and dipping times were found to be the most critical steps in making the solar cells. When the CdS layer was thin (1  $\mu\text{m}$ -2  $\mu\text{m}$ ), dipping times greater than six seconds were observed to cause shorts. Similarly, excessive heat treatment times of the thin CdS layers caused complete shorting of the cell.

It was observed that the metallic substrate used bears a great importance on the quality of the CdS films and, hence, the photocell

performance. Optimum results were obtained when the metal was inert to the depositing solution. Also, mechanical polishing of the substrate prior to dipping was observed to greatly enhance the solar cell performance.

### The CuCl Dipping Solution

The ionic composition of the cuprous chloride dipping solution was observed to critically affect the short circuit current of the solar cells. The chemical displacement reaction that takes place involves the cuprous  $\text{Cu}^+$ , and cupric  $\text{Cu}^{++}$  ions present in the solution. The greater the content of  $\text{Cu}^+$  ions is, the higher the short circuit current will be. The  $\text{Cu}^{++}$  ions produce cupric sulfide,  $\text{CuS}$ , which has detrimental effects on the photogeneration in the  $\text{Cu}_x\text{S}$  layer. The unwanted  $\text{Cu}^{++}$  ions exist in the dipping solution due to the  $\text{CuCl}$  decomposition in moist air and in water. Moisture slowly turns white  $\text{CuCl}$  into green and yellowish brown, the colors due to the formation of a green basic salt,<sup>8</sup> possibly atacamite,  $\text{CuCl}_2 \cdot 3\text{CuO} \cdot 3\text{H}_2\text{O}$ . In contact with water, the cuprous chloride is partially decomposed forming cuprous oxide and cupric chloride:



This decomposition causes the red discolorization of the  $\text{CuCl}$  solution due to formation of (red) cuprous oxide. To eliminate the unwanted  $\text{Cu}^{++}$  ions, a reducing agent,  $\text{SnCl}_2$  was introduced into the light green  $\text{CuCl}$

dipping solution. The  $\text{SnCl}_2$  reduces the cupric chloride into cuprous chloride and it was slowly added until the solution turned white. The solar cells made by dipping in this solution were observed to have short circuit currents as high as  $3 \text{ ma/cm}^2$ .  $\text{CuCl}$  dipping solutions, which were not treated with  $\text{SnCl}_2$  produced short circuit currents which were less than  $0.3 \text{ ma/cm}^2$ .

### Experimental Results

CdS deposited on copper substrates from KCN solution produced photocells with highest short circuit currents ( $1-1.5 \text{ ma/cm}^2$ ). However, the open circuit voltage was as low as 0.15 V. CdS deposited on aluminum from the ammonium solution produced cells with the highest open circuit voltage ( $V_{oc} \approx 0.3V$ ), but the short circuit current was low ( $I_{sc} = 0.1-0.3 \text{ ma/cm}^2$ ). When both methods were combined to deposit multiple layers of CdS, it was observed that lesser dips were needed to form thick layers. CdS from the ammonium solution deposits faster and thicker on metals initially coated with a CdS layer deposited from the KCN solution. The reason for this could be explained in terms of the preferential orientation of the CdS crystallites along the C-axis of the substrate. As seen from the XRD results, the KCN method yielded CdS films with growth along the C-axis only. This axis is also favorable for growths of CdS deposited from ammonium solutions, which causes faster growth and yields thicker films.

Several molybdenum, nickel and copper substrates were polished and ultrasonically washed in acetone and DI water. Seven samples of

each of the metals were then dipped in KCN depositing solution and six multiple depositions were made. The CdS layers obtained were dark orange and transparent with thickness (as measured by an aluminum step) 3-4  $\mu\text{m}$ .

The samples were then numbered in the following manner:

Molybdenum	M1 - M7
Nickel	N1 - N7
Copper	C1 - C7

M1, N1 and C1 were dipped in a hot CuCl saturated solution, 3 gm/liter at 99°C for four seconds. M2, N2 and C2 were dipped for five seconds, M3, N3 and C3 for six seconds and likewise, each of the other sets was dipped for an additional second up to 10 seconds. The cells were heat treated for 20-30 seconds at 250°C in air. This heat treatment was found to be optimum for maximum efficiency of the cells. It was observed that dipping times of 5 to 6 seconds gave highest short circuit currents. However, due to the thinness of the CdS layers, the open circuit voltages varied from 0.15 V-0.2 V. Silver paint was used to form an ohmic contact on the  $\text{Cu}_x\text{S}$  layer. However, it was noticed that the silver paint grids diffused and caused shorts which lowered the voltage to 0.1 V.

It is believed that the speed of the chemical displacement reaction of  $\text{Cu}^+$  ions into the CdS layer is  $300\text{\AA}/\text{sec}$ .<sup>9,10</sup> Therefore, a five-second dip will yield a  $1500\text{\AA}$  layer of  $\text{Cu}_x\text{S}$ , which is less than optimum ( $2000\text{\AA}$ ) for maximum photogeneration. It is well known that 99% of the electron hole pairs are generated in the  $\text{Cu}_x\text{S}$  layer and then migrate across the junction. When the cells are heat treated, cuprous

ions diffuse along the grain boundaries faster than through the bulk. If the CdS layer is not thick enough, or if the grain boundaries are continuous from the junction to the substrate, the cuprous ions could diffuse to the substrate, causing shorts. Cross-sectional samples showed  $\text{Cu}_x\text{S}$  formation down to a depth of 1-2  $\mu\text{m}$ , which is evidently the reason for low, open circuit voltage.

Solar cells with highest short circuit current were fabricated from CdS films deposited on molybdenum or nickel substrates by the following procedure: An initial coating with two multiple layers from cyanide solution followed by two multiple coatings from the conventional solutions to get a fairly thick layer. Then, three multiple layers were deposited from cyanide solution to obtain a fibrous structure of CdS. Figure 14 illustrates a typical I-V curve of one of the solar cells fabricated by this technique. The area of the cell is 1  $\text{cm}^2$ . The short circuit current, 2.7 ma, and was collected by four silver painted conductors which have lowered the open circuit voltage from an initial value of 2.0 V to 0.06 V.

Also, in Figure 14, the I-V curve of a 5  $\text{cm}^2$  solar cell is shown. This cell was fabricated by depositing six layers of CdS from KCN solution on a copper plate. The open circuit voltage, 0.04 V, initially 0.15 V, was lowered after the attachment of the silver paint grid. The open circuit current was measured at 6 ma which is an equivalence of 1.2  $\text{ma}/\text{cm}^2$ . All measurements were done on a clear day, under 1 sun illumination. Table 1 illustrates  $V_{\text{oc}}$  and  $I_{\text{sc}}$  values for solar cells fabricated by the different techniques described in this chapter.

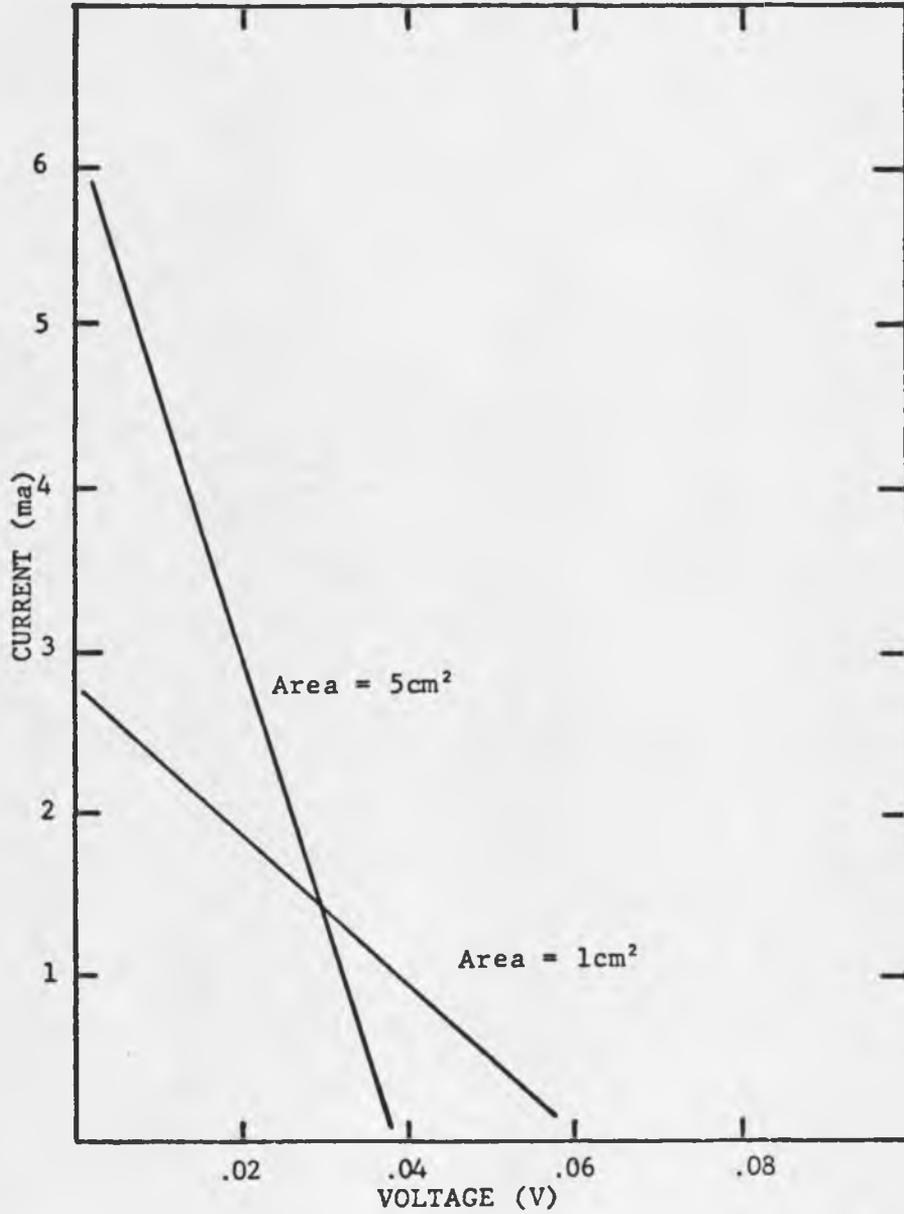


Figure 14. I-V curves of two chemically deposited solar cells under 1 sun illumination.

Table 1. A comparison between chemically deposited solar cells.

Method of Deposition of CdS	Metallic Substrate	Thickness ( $\mu\text{m}$ )	$I_{sc}$ ( $\text{ma}/\text{cm}^2$ )	$V_{oc}$ (V)	Comment
Ammonium solution	Al, Zn, Mo	8-10	0.3	0.3	6 multiple depositions
KCN-Method	Mo, Ni, CU	3-4	1-1.5	0.15	6 multiple depositions
Cd-NH <sub>4</sub> NO <sub>3</sub> Solution	Al, Zn, Mo	8-10	-	-	No observed photo-voltaic effect.
2 depositions from KCN solution + 2 depositions from ammonium solution + 3 or more dips in KCN solution	Mo, Ni	5-6	2-3	0.2	$I_{sc}$ can be increased by attaching a more efficient grid structure.

## CHAPTER 6

### CONCLUSIONS AND RECOMMENDATIONS

#### Improvement of the Solar Cells

The solar cells fabricated by the techniques described in the previous chapter have promising output capabilities. The short circuit current achievable can be as high as  $6 \text{ ma/cm}^2$  if certain improvements are done: lowering the resistivity of the CdS films; increasing the grain sizes, and attaching non-shortring grid structures. Grain sizes can be increased by slower deposition of the CdS films and/or by experimenting with the chemical parameters of the solution. Future research should be directed towards the use of chemical dopants which may lower the resistivity of the films. The I-V curves are linear which can be associated to a high series resistance. The low open circuit voltage is due to a low shunt resistance across the junction. This is mainly due to the thinness of the films. The deoposition of thicker films is expected to eliminate shorts, and increase the output current by eliminating losses across these shorts. An apparatus can be constructed to automatically and continuously supply the deposition solution which would yield films with the desired thickness and with better crystalline properties. When improved and compared to a vacuum evaporated CdS solar cell, the chemically deposited CdS solar cell could be highly competitive both in cost and simplicity of fabrication.

Discussion of Results on Impurity Analyses

Due to the lack of funds, the TEM techniques were conducted only on CdS films deposited from a solution of cadmium in ammonium nitrate. The chemical reagents used were of low chemical grades. Again, using high purity, 99.999%, chemical reagents was not possible, because no funds were available. Impurities from the chemical reagents were detected in the CdS films deposited from a solution of cadmium in ammonium nitrate. The techniques used were: Atomic Absorption Analyses and Scanning Electron Microscopy Quantitative, SEMQ. These techniques failed to reveal the nature of the three large impurity peaks as seen in Figure 9. However, they confirmed the existence of mineral impurities. The elements detected by Atomic Absorption Analyses are illustrated in Table 2; SEMQ results on CdS are in Table 3.

Table 2. Atomic absorption results on CdS deposited from a solution of Cd in ammonium nitrate.

Element		Element		Element	
N	6.49% 6.28%	Si	0.31% 0.32%	Ag	34.7 $\mu$ g/g 92.2 $\mu$ g/g
Na	3.67% 2.51%	Fe	0.22% 0.07%	Cu	29.3 $\mu$ g/g 30.0 $\mu$ g/g
C	2.63% 2.59%	Ca	0.62% 64.3 %	Cr	-- 33.5 $\mu$ g/g
H	0.49% 0.54%	K	0.12% 0.04%	Mg	77.1 $\mu$ g/g 15.3 $\mu$ g/g
				Zn	12.0 $\mu$ g/g 7.0 $\mu$ g/g
	> 10 $\mu$ g/g	Li, Rb, Ba, Sr, Mn, Ni, Ti, Al, Co, Pb, Ba			

Table 3. SEMQ results on CdS deposited from a solution of Cd in  $\text{NH}_4\text{NO}_3$ .

Energy (ev)	Area	Element and Line	
1.419	2738	Se	La
2.333	85338	S	KA
2.781	3828	Cd	LA
3.157	216418	Cd	MA
3.392	12452	Cd	MB
3.996	1915	Cd	LA
7.472	331	Ni	LA

Most of these minerals were listed on the containers of the reagents and, thus, it will be quite important to conduct the same analyses techniques on samples prepared by using high purity reagents. It would be quite interesting to see the x-ray diffraction pattern of CdS films deposited from a solution of highly pure cadmium in ammonium nitrate, and to check for the three impurity peaks. If these impurity peaks were to be present, then an important conclusion would be made: that the chemical reaction which takes place is solely a characteristic property of the method of deposition.

#### Guidelines for Further Study

It is recommended that further experimentation be conducted on CdS and ZnO films deposited from high purity chemical reagents. Principally, the films should be characterized using TEM, SEMQ, XRD,

Emission Spectroscopy and Atomic Absorption analysis techniques. These techniques should also be utilized to study impure films deposited from the conventional and KCN solutions and compare the results with those already obtained.

Further characterization of the films, deposited from pure and impure chemical reagents, should include the measurement of the following parameters: electron and hall mobilities, carrier lifetime, carrier concentration, resistivity, diffusion length, and absorption coefficient. These measurements would be used as guidelines to determine the effects of impurities on the chemically deposited solar cell performance.

The above mentioned suggestions are essential for providing a semi-complete study of the crystalline, the chemical composition, and the semiconducting properties of the chemically deposited CdS films. This study would be complete, when the effects of the metallic substrates on the deposition reaction and on the film composition are investigated. Based on all the results obtained, a full technical and economical evaluation of the chemically deposited solar cells can then be carried out. If high purity reagents would make the cell too expensive to fabricate, then the research should be directed toward finding the allowable level of impurities in the chemical reagents, which would make the fabrication more economic.

Some other guidelines for further research are listed:

1. The chemical deposition of CdSe (using the new techniques, and selenourea as a seleniding agent), should be investigated.

2. A wide search for chemical solutions, which would dissolve metals forming suitable complexes capable of depositing adhesive films of the metallic sulfides, should be carried out.

3. The previous suggestion should be accompanied by a wide search for suitable sulfiding agents. HgS was successfully deposited from solution by dissolving freshly precipitated HgO in KCN solution; however, the films deposited were not adhesive when either thiourea or thioacetamide were added. A search for sulfiding agents with stronger bonding energies (with the S ion) may lead to the deposition of adhesive films of HgS. Thioacetamide, for example, does not yield adhesive films of CdS, when it is added to the cyanide solution. However, when it is added to the ammonium solution (conventional), it yields adhesive films of high orientational growth as shown in Figure 11. This illustrates the importance of the role which the organic complex plays during deposition.

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3605 5